Electrical Properties of Block Copolymers Containing Silver Nanoclusters Within Oriented Lamellar Microdomains

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ABSTRACT: Films containing silver nanoclusters within a lamellar morphology were obtained via postprocessing reduction of the silver-containing regions of block copolymers synthesized by ring opening metathesis polymerization. Solution-cast films (0.1 mm thickness) of the block copolymer exhibited an oriented lamellar morphology with lamellar normals perpendicular to the film plane. The slightly anisotropic dielectric properties, perpendicular and parallel to the film plane, were investigated by direct measurement and by model calculations. The conductivity was highly anisotropic, differing by at least four orders of magnitude in directions parallel and perpendicular to the film plane. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 723–729, 1997

INTRODUCTION

Metal nanoclusters are of great interest because they can have physical and chemical properties that are characteristic of neither the metal atoms nor the bulk metal. Quantum size effects and the large ratio of surface area to volume can contribute to some of the unique properties of metal nanoclusters.[1–5] Such clusters are expected to have interesting electrical and optical properties.[6,7] Ishizu et al.[8] studied the conductivity of a poly(styrene-*b*-2-vinylpyridine) block copolymer which formed horizontally oriented lamellar microdomains containing colloidal silver. They found that the conductivity of the film was highly anisotropic, differing by about six orders of magnitude in directions parallel and perpendicular to the film plane.

Recently we reported a method of synthesizing metal nanoclusters within the microdomains of block copolymers prepared by ring opening metathesis polymerization (ROMP).[9–11] Our technique to synthesize nanoclusters takes advantage of the self-assembled microdomain structure of block copolymers, inside which nanoclusters can be made in a controlled manner.

In this article films containing silver nanoclusters were prepared by static solution casting and exhibited horizontally oriented lamellar domains. The morphologies of the block copolymers and nanoclusters were characterized by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD). The dielectric properties and anisotropic conductivity of the static-cast films were also investigated.

EXPERIMENTAL

All monomers were prepared as described in the literature.[9–11] $[NORPHOS]_{60}[MTD]_{300}$ (NORPHOS = racemic 2-*exo*-3-*endo*-bis(diphenylphosphino)-bicyclo[2.2.1]heptane; MTD = methyltetracyclododecene) was synthesized using the Schrock initiator as described elsewhere.[9,10] After introducing two equivalents of Ag(Hfacac)(COD)[9,10] (Hfacac

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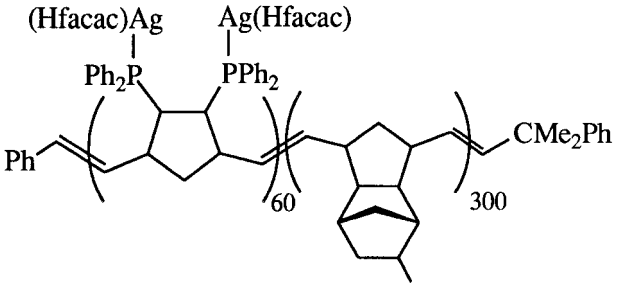

Figure 1 $[Ag]_{60}[MTD]_{300}$.

= hexafluoroacetylacetonate; COD = 1,5-cyclooctadiene) per NORPHOS, $[Ag_2(Hfacac)_2(NORPHOS)]_{60}[MTD]_{300}$ ($[Ag]_{60}[MTD]_{300}$) was prepared (Fig. 1). Homopolymers of $[MTD]_{300}$ and $[Ag_2(Hfacac)_2(NORPHOS)]_{80}$ ($[Ag]_{80}$) were prepared in the same way.

Films of $[Ag]_{60}[MTD]_{300}$ and $[MTD]_{300}$ ($\sim$ 100 μm thick) were static cast from a 3 wt % toluene solution on Teflon-coated aluminum cups under nitrogen in the dark. The toluene was allowed to evaporate slowly over a period of 5–8 days. The films obtained were further dried under vacuum for at least 2 days. In the case of spin coating, solution of 3 wt % of $[Ag]_{80}$ in toluene was spin-coated onto glass slides or onto aluminum-coated quartz slides at 2000 rpm for 60 s under argon. The spin-coated film (1000 Å thick) was dried under vacuum for at least 24 h.

To make silver nanoclusters within the microdomains, the films containing silver complexes were heated to 120°C for 24 h under vacuum. After reduction the film was further evacuated at room temperature for at least 24 h.

An LKB Ultratome III Model 8800 was used to obtain ultrathin samples ($\sim$ 50 nm thick) for TEM. The spin-coated film was directly transferred onto a copper grid. TEM was performed on a JEOL 200 CX operating at 200 kV.

The orientation of the lamellar morphology was studied by SAXS using a Rigaku instrument with a 1.54 Å CuK_α rotating-anode point source, Charles Supper double mirror focusing optics, and a Nicolet two-dimensional detector. For WAXS experiments, the CuK_α radiation was filtered using a thin Ni filter and X-ray diffraction data were obtained through DMAXB Rigaku-USA software. The slit system allowed collection of the diffracted beam with a divergence angle of less than 0.2°.

Dielectric measurements were performed with a Hewlett Packard 4284A Precision LCR meter controlled by a 386 PC computer at frequencies ranging from 500 Hz to 1 MHz at room temperature. This instrument has a frequency range of 20 Hz to 1 MHz, but frequencies below 500 Hz were not used because of the unfavorable signal-to-noise ratio found at lower frequencies.[12] Round electrodes of gold or aluminum were thermally evaporated on each side of the film. A spin-coated film was prepared on aluminum-coated quartz slides and round aluminum electrodes were deposited on top of this film. The thickness of spin-coated films was measured using a Dektak 8000. The electrode-diameter-to-film-thickness ratio was kept above 100 so that the effect of fringe fields was negligible.[12] Polystyrene and PMMA were used as standards to verify the dielectric measurements.

The conductivity perpendicular to the film plane was calculated from the resistance measured by a Keithley electrometer using the parallel-plate structure.[13] Also, near-DC conductivity (very low frequency) was estimated by extrapolation from AC measurement using a Hewlett Packard 4284A Precision LCR meter. A four-point conductivity measurement parallel to the film plane was carried out according to the method of van der Pauw,[13,14] employing a Keithley digital programmable current source and digital DC voltmeter. A gold wire was attached with conductive carbon paste at each corner of rectangular samples (approximate dimensions of $0.1 \times 5 \times 10$ mm). In the case of spin-coated films, in-plane conductivity was also measured using the four-point method.

RESULTS AND DISCUSSION

Characterization

A static-cast film of $[Ag]_{60}[MTD]_{300}$ showed lamellar morphology (Fig. 2). The silver-containing

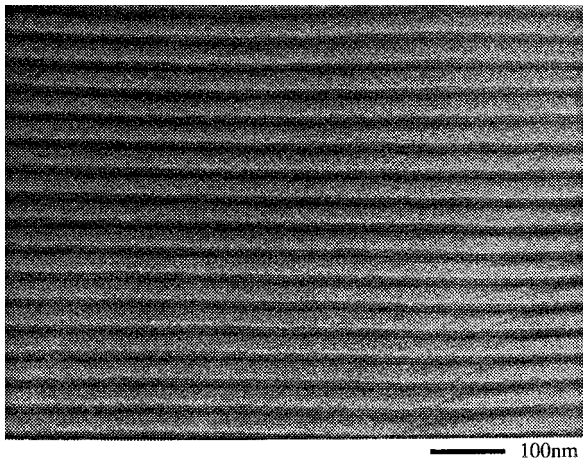

Figure 2 Transmission electron micrograph of $[Ag]_{60}[MTD]_{300}$.

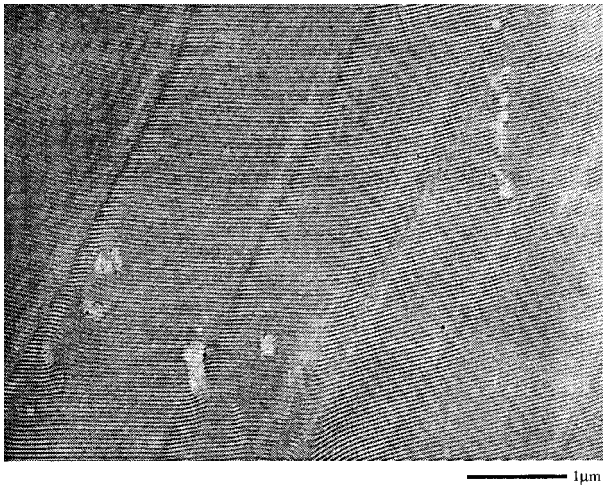

Figure 3 Transmission electron micrograph of $[Ag]_{60}[MTD]_{300}$ (low magnification).

microdomains appear as darker regions. The low-magnification TEM micrograph (Fig. 3) exhibited not only a locally well-ordered but a long-range oriented morphology. Oriented lamellar morphologies induced by the interaction between substrates and block copolymers have been reported.[8,15–17] This long-range orientation was examined by SAXS. In Figure 4, two-dimensional SAXS patterns obtained with the X-ray beam aligned perpendicular to the film plane [Fig. 4(a)] and parallel to the film plane [Fig. 4(b)] are shown. If all lamellar microdomains were perfectly oriented parallel to the film plane, there would be no X-ray scattering in the direction perpendicular to the film, and a two point spot-like scattering along the vertical axis would appear in a SAXS pattern parallel to the film plane. However, the SAXS pattern perpendicular to the film plane [Fig. 4(a)] exhibited two rings, and the SAXS pattern parallel to the film plane [Fig. 4(b)] showed a first-order ring and a second-order arc, in which stronger scattering intensities appeared along the vertical axis. These results indicate that most, but not all, lamellar planes are parallel to the film plane.

The $[Ag]_{60}[MTD]_{300}$ film with oriented lamellar morphology was thermally treated to form clusters. The TEM micrograph after reduction (Fig. 5) showed that silver nanoclusters (~8 nm in diameter) formed predominantly within the original silver-containing microdomains. The cluster formation was confirmed by WAXS analysis. Before thermal treatment, only a broad peak at low scattering angle appeared, which can be attributed to the amorphous polymer [Fig. 6(a)]. The WAXS profile of the thermally treated film showed five new peaks, which correlate with the expected spacing for crystalline silver in its cubic form [Fig. 6(b)].

Dielectric Properties

The dielectric properties perpendicular to the film plane of the static-cast film of $[Ag]_{60}[MTD]_{300}$ containing silver nanoclusters (Fig. 5) were studied using a parallel-plate structure. Figure 7 shows dielectric constants (ε') and loss tangents ($\tan \delta$) as a function of frequency. The values of the dielectric constant ($\varepsilon' \approx 3.5$) were essentially invariant over the entire range of frequencies. The loss tangents also showed values < 0.03 over the range of frequencies tested. The $[Ag]_{60}[MTD]_{300}$ contains 30 wt % silver within microdomains, and 14 wt % silver overall. The volumetric loading of silver clusters inside the lamellar domains is ~4.3 vol %, assuming that the densities of polymer and silver are 1.0 and 10.5 g/cm^3, respectively. The dielectric constants observed are reasonable for the silver concentration value according to the classical model of a composite of metal occlusions in a nonconductive matrix.[7] Since the static-cast film of $[Ag]_{60}[MTD]_{300}$ has an anisotropic structure consisting of oriented lamellae, it is interesting to compare dielectric properties parallel and perpendicular to the film plane. In practice, however, it is not easy to measure dielectric properties parallel to the film plane because the film is only ~100 μm thick. But if we know the dielectric constant of each block, we can calculate the dielectric constant parallel to the film plane ($\varepsilon'_{\parallel}$) and confirm the measured value of the dielectric constant perpendicular to the film plane ($\varepsilon'_{\perp}$). $\varepsilon'_{\perp}$ can be modeled as a series combination of the dielectric constant of the [Ag] block (ε'_{Ag}) and the dielectric constant of the [MTD] block (ε'_{MTD}) (Fig. 8). Also, $\varepsilon'_{\parallel}$ can be modeled as a parallel combination of ε'_{Ag} and ε'_{MTD} (Fig. 8). To avoid the contribution of interfacial polarization, which is dominant at low frequencies, $\varepsilon'_{\perp}$ and $\varepsilon'_{\parallel}$ are calculated at 10^4 Hz. From series and parallel combinations of blocks (Fig. 8), we can write

$$1/\varepsilon'_{\perp} = (t_{Ag}/t)/\varepsilon'_{Ag} + (t_{MTD}/t)/\varepsilon'_{MTD} \quad (1)$$

$$\varepsilon'_{\parallel} = (t_{Ag}/t)\varepsilon'_{Ag} + (t_{MTD}/t)\varepsilon'_{MTD} \quad (2)$$

where t is the total thickness ($t = t_{Ag} + t_{MTD}$), t_{Ag} is the thickness of [Ag] domains, and t_{MTD} is the

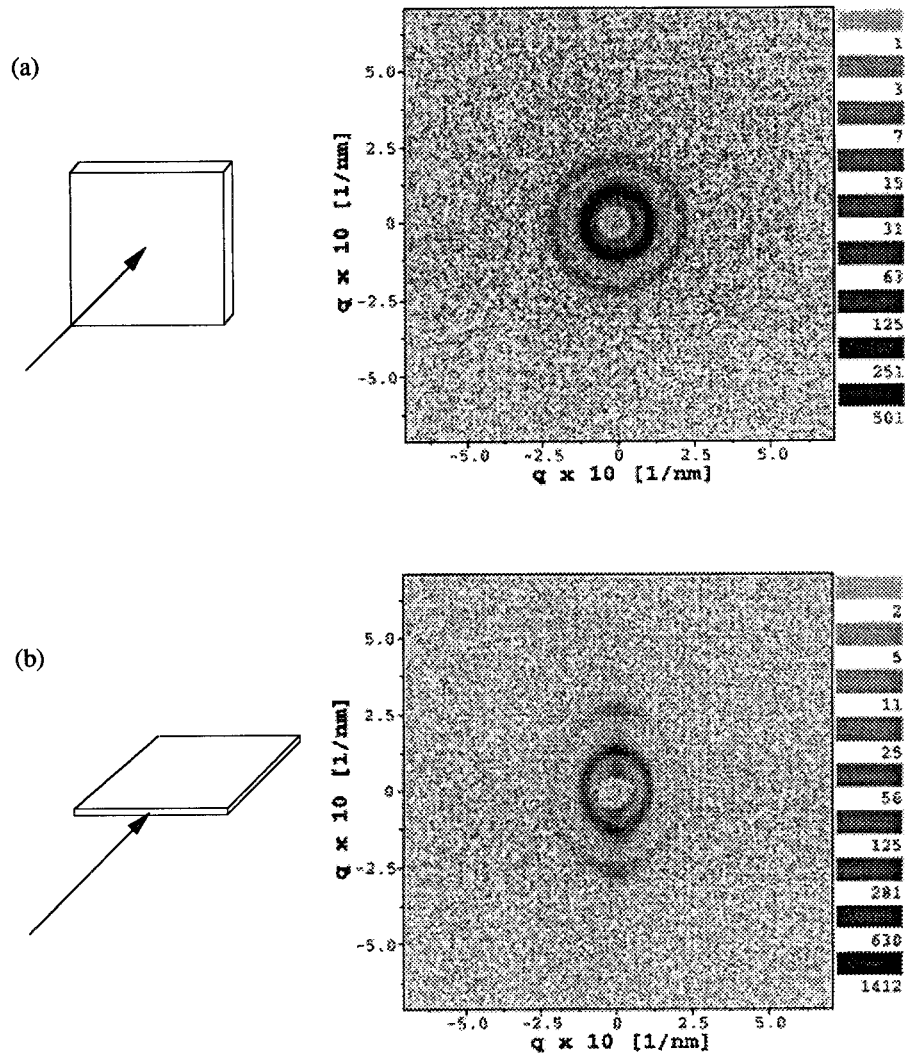

Figure 4 Two-dimensional SAXS patterns of $[Ag]_{60}[MTD]_{300}$. (a) Perpendicular to the film plane; (b) parallel to the film plane.

thickness of [MTD] domains. From the TEM micrographs (Figs. 3 and 5), we can find $t_{Ag}/t = 0.455$ and $t_{MTD}/t = 0.545$. ε'_{MTD} was measured in the same way as $\varepsilon'_{\perp}$ and is equal to 2.88 at 10^4 Hz. For the ε'_{Ag} measurement, we were unable to use static-cast films of the homopolymer of [Ag] because such films were very brittle, making it impossible to deposit electrodes on both sides of the film for dielectric measurements. Also, when clusters were formed in a static-cast film of the metal-containing homopolymer, the cluster formation was not well controlled, and very large size clusters with a broad size distribution were obtained.[11] We believe that interfaces between blocks play an important role in the nucleation and growth of clusters in block copolymers.[18] Because there are no such interfaces in a film of homopolymer of [Ag], the size and size distribution of clusters in a film of homopolymer of [Ag] are quite different from those in the $[Ag]_{60}$-$[MTD]_{300}$ block copolymer. The better control over cluster size and the improved mechanical performance are compelling reasons for employing block copolymers instead of homopolymers to obtain controllable clusters in a physically useful film.

The spin-coating technique was employed to obtain an appropriate specimen for measuring ε'_{Ag}. A slightly higher molecular weight homopolymer ($[Ag]_{80}$) was used. A thin spin-coated film of $[Ag]_{80}$ was transferred onto a copper grid for TEM and thermally treated for cluster formation. Before cluster formation, there was no visible contrast in the TEM micrograph. After cluster formation, relatively small (~5 nm in diameter), irreg-

Figure 5 Transmission electron micrograph of $[Ag]_{60}$-$[MTD]_{300}$ after cluster formation.

ularly shaped clusters were obtained (Fig. 9). Since the thickness of the spin-coated film was of the same order of magnitude as the dimension of the lamellae in the block copolymers, this film can be considered analogous to a single lamellae of the [Ag] block in $[Ag]_{60}[MTD]_{300}$. Thus, the free surface of the thin film and/or the interface between the film and substrate can play a similar role as the interface between blocks in block copolymers, so that evenly distributed clusters were produced in the spin-coated film of $[Ag]_{80}$. Therefore, we take the spin-coated film of $[Ag]_{80}$ as a substitute for dielectric measurements of a single lamella of the [Ag] block. A parallel-plate structure was prepared for a spin-coated film of $[Ag]_{80}$ as described in the experimental section. A value of $\varepsilon'_{Ag} = 4.80$ was obtained at 10^4 Hz.

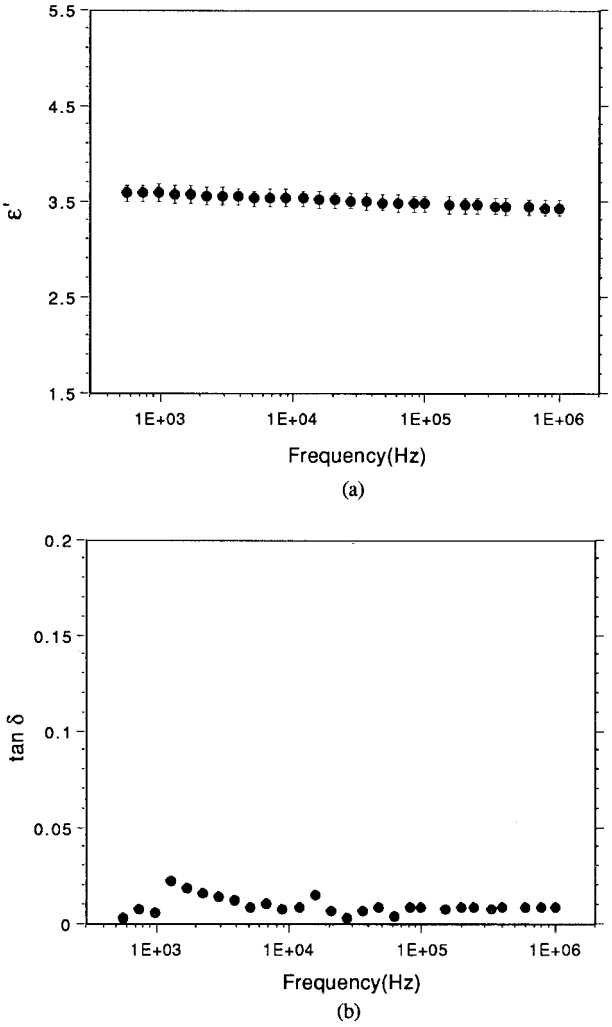

Figure 7 Dielectric properties perpendicular to the film plane of $[Ag]_{60}[MTD]_{300}$ containing silver nanoclusters. (a) ε' versus frequency; (b) tan δ versus frequency.

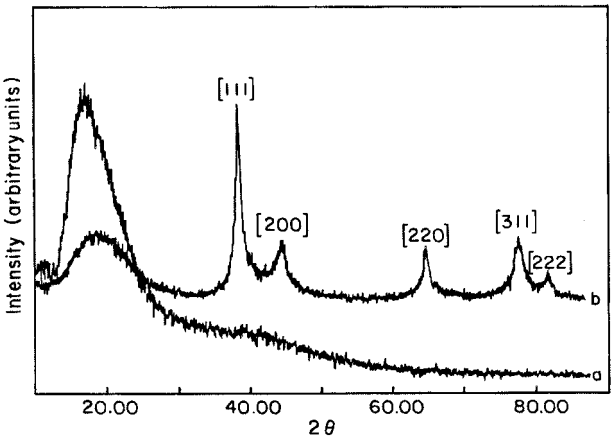

Figure 6 WAXS profiles of $[Ag]_{60}[MTD]_{300}$. (a) Before cluster formation; (b) after cluster formation.

The array of experimentally derived values $\{\varepsilon'_{Ag}$ (4.80), ε'_{MTD} (2.88), t_{Ag}/t (0.455), and t_{MTD}/t (0.545)$\}$ can be inserted into eqs. (1) and (2). From eq. (1), the calculated value of $\varepsilon'_{\perp}$ is 3.52, essentially identical with the measured value of $\varepsilon'_{\perp}$ at 10^4 Hz in Figure 7. From eq. (2), $\varepsilon'_{\parallel}$ is 3.76, which cannot be measured experimentally. The dielectric constants for the static-cast film of

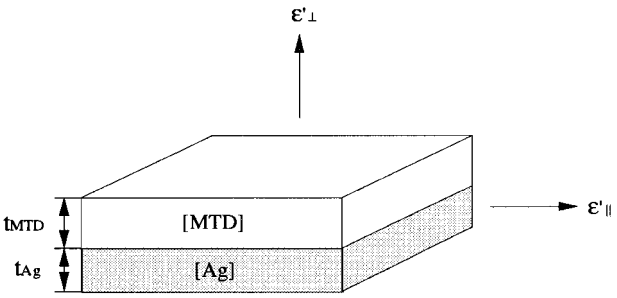

Figure 8 Schematic representation of the oriented lamellae of $[Ag]_{60}[MTD]_{300}$.

$[Ag]_{60}[MTD]_{300}$ showed only a slight anisotropy ($\varepsilon'_{\perp} = 3.52$, $\varepsilon'_{\parallel} = 3.76$).

Conductivity

Electrical conductivity measurements of a static-cast film of $[Ag]_{60}[MTD]_{300}$ were performed. The conductivity perpendicular to the film plane ($\sigma_{\perp}$) was measured using the same parallel-plate structure of the dielectric measurements. In DC measurements $\sigma_{\perp}$ was below the detection limit (10^{-13} S/cm) of our instrument. However, we can estimate near-DC conductivity (very low frequency) by extrapolation from AC measurements. The value of $\sigma_{\perp}$ (2.2×10^{-15} S/cm) in Table I was obtained by extrapolating AC results to 10^{-3} Hz. The conductivity parallel to the film plane ($\sigma_{\parallel}$) was measured using the four-point method described earlier. The values of $\sigma_{\parallel}$ are $\sim 10^{-9}$ S/cm. The order of magnitude of $\sigma_{\parallel}$ is reasonable when the silver content (30 wt % within microdomains) is considered.[8,19] Comparing $\sigma_{\parallel}$ with $\sigma_{\perp}$, the $[Ag]_{60}[MTD]_{300}$ film has a relatively highly anisotropic conductivity, differing by at least four orders of magnitude.

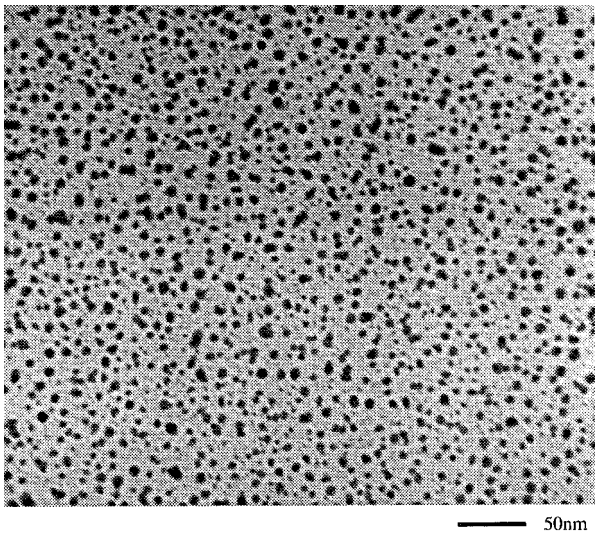

Figure 9 Transmission electron micrograph of the spin-coated film of $[Ag]_{80}$ after cluster formation.

Table I Conductivities of the Static Cast Film of $[Ag]_{60}[MTD]_{300}$ Containing Silver Nanoclusters

$\sigma_{\perp}$ (S/cm)	$\sigma_{\parallel}$ (S/cm)
$<10^{-13}$ (2.2×10^{-15})[a]	3.4×10^{-9}

[a] Obtained by extrapolation to 10^{-3} Hz from AC measurements.

We can find the upper and lower limit of the conductivity of the $[Ag]_{60}[MTD]_{300}$ film by measuring the conductivities of homopolymers of [Ag] and [MTD], respectively. The conductivity of $[MTD]_{300}$ was $<10^{-13}$ S/cm (1.2×10^{-15} at 10^{-3} Hz). This value is of the same order of magnitude as $\sigma_{\perp}$. This indicates that the conducting path perpendicular to the film plane is fully interrupted by the [MTD] block, so that $\sigma_{\perp}$ was of the same order of magnitude as the conductivity of $[MTD]_{300}$. For the conductivity measurement of a homopolymer of [Ag], the spin-coating technique was used for the same reasons as were explained for the dielectric measurements. The conductivity of the spin-coated film of $[Ag]_{80}$ containing silver nanoclusters was $\sim 1.0 \times 10^{-8}$ S/cm. This is an order of magnitude higher than $\sigma_{\parallel}$. Since the lamellae of the silver-containing block in the $[Ag]_{60}[MTD]_{300}$ film were not perfectly oriented with the film plane, as SAXS results indicate in Figure 4, the spin-coated film of $[Ag]_{80}$ could represent a perfectly oriented single lamellae and its conductivity could be the upper limit of $\sigma_{\parallel}$. Thus, the experimental result showed that $\sigma_{\parallel}$ was well bounded by the conductivity of $[Ag]_{80}$.

CONCLUSION

The $[Ag]_{60}[MTD]_{300}$ film prepared by static casting exhibited well-oriented lamellar morphology parallel to the film plane, which was confirmed by TEM and SAXS experiments. A dielectric study of the films revealed classical behavior for particle-filled systems and $\varepsilon'_{\perp}$ was measured experimentally and the result was consistent with the calculation based on the dielectric constant of each block. Also, the calculation gave $\varepsilon'_{\parallel}$ for this

film. At least a four-order-of-magnitude anisotropy in the conductivity of this film was found by conductivity measurements.

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